



PATENT APPLICATION  
STC-03-0010

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re application of: Scott F. Mitchell  
Gopalakrishnan Juttu  
Robert Scott Smith

Serial No.: 10/748,418

Group Art Unit: 1764

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Examiner: Thuan D. Dang

For: Process for Alkane Aromatization Using Platinum-Zeolite Catalyst

Commissioner for Patents  
P.O. Box 1450  
Alexandria, Virginia 22313-1450

AFFIDAVIT UNDER 37 CFR §1.132

Scott F. Mitchell, being duly sworn, deposes and says that:

I am a scientist for SABIC Americas, Inc., at the SABIC Technology Center in Sugar Land, Texas.

My educational background is as follows: I hold a Bachelor of Science degree in Chemical Engineering from the University of Pennsylvania granted in 1983, a Master of Science degree in Chemical Engineering from the University of Pittsburgh granted in 1987 and a Doctor of Philosophy degree in Chemical Engineering from the University of Pittsburgh granted in 1987.

My duties at the SABIC Technology Center include research in the field of catalytic reaction of an alkane using a zeolite catalyst to produce aromatics, including the synthesis and evaluation of catalysts such as those disclosed in the U.S. patent no 4,891,663 to Chu ("Chu").

I have worked in the field of catalysis, both in industry and in academia, for approximately twenty years. I am the author or co-author of approximately seven articles on the subject and have approximately five patents issued or patent applications pending naming me as an inventor or co-inventor in this field. I am an invited reviewer for the National Science Foundation, the Journal of Catalysis, the AIChE Journal and Applied Catalysis.

In view of my qualifications as specified above, I consider myself to be an expert in the art of alkane aromatization and related catalysts, specifically the catalytic reaction of an alkane using a zeolite catalyst to produce aromatics. I have read the Office Action of March 9, 2005, for the above identified patent application and I have reviewed and am familiar with the subject matter disclosed in U.S. patent no 4,891,663 to Chu ("Chu").

The following Examples and Comparative Example illustrate a catalyst of the claimed invention compared to those of the cited Chu patent.

Example 1: Pt/ZSM-5

35.7 grams of HiQ-40 (Alcoa alumina) were combined with a small amount (i.e., a few drops) of 70 wt% nitric acid reagent grade to peptize the alumina. The powder was mixed thoroughly until all of the acid was absorbed and the powder was free flowing and free of clumps. 50 grams of CBV 15014 Zeolyst ZSM-5 zeolite was added and the dry powders were mixed together. Approximately 20 ml of deionized water were added gradually to the powder while mixing. The mixture was kneaded until a uniform dough is obtained. The dough was divided into uniform balls of approximately ½ inch in diameter. The balls were placed in a pan and dried in an oven overnight at 100 C. After the balls were dry, they were calcined in a muffle furnace with flowing air (100cc/min) according to the following protocol.

Room temperature to 550C @ 1C/min, then held 5 hours.

Cooled to room temperature.

After the sample was cooled, it was crushed and sieved to 20-40 mesh.

30 grams of the crushed and sieved material were combined with 100 ml of 0.05M  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$  (Aldrich) solution. This solution was allowed to remain in contact with the solid material for at least 20 hours. After this period of time, the liquid was decanted and the process was repeated twice more. The resultant catalyst precursor was washed with DI water, dried in an oven at 90C overnight, then calcined in a muffle furnace with 10% flowing air in nitrogen (100cc/min) according to the following protocol.

Room temperature to 300C @ 1C/min, then held 4 hours.

Cooled to room temperature.

#### Example 2: Pt/ZSM-5

35.7 grams of HiQ-40 (Alcoa alumina) were combined with a small amount (i.e., a few drops) of 70 wt% nitric acid reagent grade to peptize the alumina. The powder was mixed thoroughly until all of the acid was absorbed and the powder was free flowing and free of clumps. 50 grams of CBV 8650 Zeolyst ZSM-5 zeolite was added and the dry powders were mixed together. Approximately 20 ml of deionized water were added gradually to the powder while mixing. The mixture was kneaded until a uniform dough is obtained. The dough was divided into uniform balls of approximately ½ inch in diameter. The balls were placed in a pan and dried in an oven overnight at 100 C. After the balls were dry, they were calcined in a muffle furnace with flowing air (100cc/min) according to the following protocol.

Room temperature to 550C @ 1C/min, then held 5 hours.

Cooled to room temperature.

After the sample was cooled, it was crushed and sieved to 20-40 mesh.

30 grams of the crushed and sieved material were combined with 110 ml of 0.02M  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$  (Aldrich) solution. This solution was allowed to remain in contact with the solid material for at least 20 hours. After this period of time, the liquid was decanted and the process was repeated twice more. The resultant catalyst precursor was washed with DI water, dried in an oven at 90C overnight, then calcined in a muffle furnace with 10% flowing air in nitrogen (100cc/min) according to the following protocol.

Room temperature to 300C @ 1C/min, then held 4 hours.

Cooled to room temperature.

#### Example 3: Pt/Ga-ZSM-5 (Pt/Ga/ZSM-5)

25.08g of CBV5524 (ZSM-5 with  $\text{SiO}_2/\text{Al}_2\text{O}_3 \sim 55$ ; Zeolyst Inc.) were combined with 6.43g of Ultrasil VN3SP (amorphous precipitated silica; Degussa) in a ceramic crucible. 40g of Ludox TM-50 (50wt% colloidal silica; Aldrich) were added to the above mixture and mixed well. Deionized (DI) water was added to the mixture which was worked into a homogeneous dough. The dough was dried at 90°C for 4 hours and then calcined in a muffle furnace with air flow at 550°C for 6 hours.

The calcined material was crushed and sieved to 20/40 mesh. The sized material was ion exchanged with 0.5M  $\text{NH}_4\text{NO}_3$  solution at 60°C. The solution was decanted and the solids were washed with DI water. The ion exchange was repeated two more times. The solid material was

dried at 90°C for 4 hours and then calcined in a muffle furnace with air flow at 550°C for 6 hours.

3.5g of gallium nitrate hydrate (Aldrich) were dissolved in 25ml DI water. 26.53g of the solid material from above was impregnated with this gallium solution. The solid material was dried at 90°C for 4 hours and then calcined in a muffle furnace with air flow at 550°C for 6 hours.

0.083g of tetraamine platinum (II) nitrate (Alfa-Aesar) was dissolved in 22ml of DI water. 22.32g of the solid material from the step above were impregnated with the platinum solution, dried at 90°C for 4 hours and then calcined in a muffle furnace with air flow at 300°C for 6 hours.

#### Example 4: Pt/Ge-ZSM-5

20 g of 274-076 Ge-ZSM-5 were combined with 4.44g of Ultrasil VN3SP (amorphous precipitated silica; Degussa) in a ceramic crucible. 32g of Ludox TM-50 (50wt% colloidal silica; Aldrich) were added to the above mixture and mixed well. Deionized (DI) water was added to the mixture and worked it into homogeneous dough. The dough was dried at 90°C for 4 hours. The solid material was crushed and sized to 20/40 mesh. The sized material was ion exchanged with 0.5M  $\text{NH}_4\text{NO}_3$  solution at 60°C. The solution was decanted and washed with DI water. The ion exchange was repeated two more times. The solid material was dried at 90°C for 4 hours and then calcined in a muffle furnace with air flow at 550°C for 6 hours.

20.35 grams of the above material were combined with a 0.005M  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$  aqueous solution for three hours. The solution was decanted and the solids were washed with DI

water, dried in an oven at 90C overnight and then calcined in a muffle furnace with air flow at 300°C for 5 hours.

A Comparative Example for a catalyst containing gallium-ZSM-5 on which no other metal was deposited was prepared as follows:

Comparative Example 1: Ga-ZSM-5 (**Ga/ZSM-5**)

51.4 grams of HiQ-40 (Alcoa alumina) were combined with a small amount (i.e., a few drops) of 70 wt% nitric acid reagent grade to peptize the alumina. The powder was mixed thoroughly until all of the acid was absorbed and the powder was free flowing and free of clumps. 40.5 grams of CBV 5524 Zeolyst ZSM-5 zeolite was added and the dry powders were mixed together. Approximately 20 ml of deionized water were gradually added to the powder while mixing. The mixture was kneaded until a uniform dough was obtained. The dough was divided into uniform balls of approximately ½ inch in diameter. The balls were placed in a pan and dried in an oven overnight at 100 C. After the balls are dry, they were calcined in a muffle furnace with flowing air (100cc/min) according to the following protocol.

Room temperature to 300C @ 3C/min, then held 3 hours.

300C to 550C @ 2C/min, then held 6 hours.

Cooled to room temperature.

After the sample was cooled, it was crushed and sieved to 20-40 mesh.

39.36 grams of the crushed and sieved material were combined with a solution of 20 ml of deionized water into which 3 grams of gallium nitrate (Aldrich) had been dissolved. The resultant mixture was dried in an oven at 100C for 2 hours, then calcined in a muffle furnace

with flowing air (100cc/min) according to the following protocol.

Room temperature to 300C @ 3C/min, then held 3 hours.

300C to 550C @ 2C/min, then held 6 hours.

Cooled to room temperature.

For each of the catalysts from the Example and Comparative Examples above, unless specified otherwise, 4g of the sized catalyst (20-40 mesh) was loaded into the reactor and reduced at 400°C under 50-50 H<sub>2</sub>/N<sub>2</sub> stream (total flow rate = 60ml/min) for 4 hours. The catalyst was then sulfided with 1vol% H<sub>2</sub>S (remainder N<sub>2</sub>) until there was a breakthrough of H<sub>2</sub>S (typically 1.5 hours). The catalyst was then swept with 50-50 H<sub>2</sub>/N<sub>2</sub> stream for 1 hour. Propane was then introduced into the reactor at 34 ml/min with the reactor ramped to the desired reaction temperature (typically 500°C). The reactor was held at 22 psig pressure during the reaction.

The results are summarized in the Table below

Table

	Reaction time (minutes)	Conversion (%)	BTX Selectivity (%)	Fuel Gas C1 (%)	Fuel Gas C2 (%)
Example 1	313	53.7	40.9	4.5	42
Example 2	313	76.3	34.7	6.4	54.9
Example 3	311	59.6	40.8	12.9	41.5
Example 4	308	57.2	56.9	4.7	30.3
Comparative Example 1	279	60.5	39.8	26.1	26

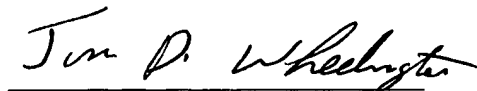
As can be seen from these results, a catalyst of a ZSM-5 on which platinum has been deposited has better performance in a process for the aromatization of alkanes than that for a catalyst of a gallium-ZSM-5 on which no metal had been deposited. In a process for the aromatization of alkanes a catalyst of ZSM-5 (which may contain only aluminum or silicon or which may have germanium substituted for silicon or gallium substituted for aluminum) on which platinum has been deposited suppresses the formation of methane relative to ethane better than a catalyst of ZSM-5 which has gallium substituted for aluminum on which platinum has not been deposited.

Further deponent saith not.

IN TESTIMONY WHEREOF, I have hereunto set my hand and affix my signature this  
11 day of July, 2005.

  
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Scott F. Mitchell

On this 11<sup>th</sup> day of July, 2005, personally appeared before me,  
Scott F. Mitchell, known to me to be the person who executed the foregoing affidavit and  
acknowledged the same to be her free act and deed.

  
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Notary  
My Commission expires June 7, 2009

